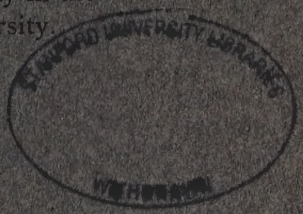
FACTORS AFFECTING THE STABILITY OF ADDITION COMPOUNDS IN SOLUTION AND THEIR INFLUENCE UPON VISCOSITY

by

ELIZABETH BRAKELEY, B.A., M.A.

DISSERTATION

Submitted in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy in the Faculty of Pure Science of Columbia University.



NEW YORK CITY, 1920

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Nichols Laboratories of Inorganic Chemistry,
Columbia University, February, 1920.

FACTORS AFFECTING THE STABILITY OF ADDITION COMPOUNDS IN SOLUTION AND THEIR INFLUENCE UPON VISCOSITY

INTRODUCTION

In the development of our knowledge of conditions existing in nonaqueous solutions of finite concentrations, various complicating factors are introduced which make quantitative determinations exceedingly difficult. The effect of compound formation between solvent and solute and of complex ion formation upon the equilibrium existing in the solution must be carefully examined before any definite conclusions can be drawn.

In several preceding articles[1] of this series the hypothesis has been advanced that ionization in solutions is preceded by the formation of complexes between solvent and solute and that the decomposition of these into ions is caused by a weakening of the electrostatic attraction existing between the constituent radicals. It will be well to summarize the theory advanced in these papers in order to present more clearly the conclusions drawn from this research. In the nonaqueous solutions examined it was found that the extent of ionization depends upon:

(1) the extent of compound formation, or the degree to which the reaction $AB+CD \rightleftarrows AB \cdot CD$ proceeds from left to right; and
(2) the extent of dissociation of these compounds into ions of opposite charge, or the degree to which the reaction $AB \cdot CD \rightleftarrows (AB \cdot C)^{+}+D^{-}$ proceeds from left to right.

It has been found to be a general rule that the complexity and the stability of the addition compounds increase uniformly with the difference in character of the compounds AB and CD. That is to say, an increase in the acidic character of the compound AB and in the basic character of CD favors more stable compound formation. Complexes other than those of the type

[1] Kendall, Booge and Andrews, J. A. C. S., 39, 2302 (1917).
Kendall and Booge, J. A. C. S., 39, 2326 (1917).

AB·CD are found only when AB and CD are decidedly diverse. This rule applies in the case of pure liquids as well as with solutions. The more diverse the character of the two radicals of the compound, the more readily will association take place. In the ionization of pure liquids it has been found that the higher the degree of association, the less firmly are the constituent groups of the complex molecules held together and the more readily will disintegration into ions of opposite charge take place. Therefore, it is concluded that self-ionization is characteristic of highly associated liquids.

In the ionization of solutions various results may be obtained, depending upon the character of the two compounds. First, a mixture of two ideal saturated substances, such as two hydrocarbons, gives a solution of no conductivity. Second, a solution of an unsaturated substance in a saturated substance gives a solution of conductivity less than that of the components when pure since the degree of association of the solute decreases with decreasing concentration. Third, the mixture of two unsaturated substances affords three types of results depending upon the character of the compounds. In the first case, the conductivity of the mixture is not greater than that of the pure substances, when the two components are similar in character, and therefore there is no compound formation. The chief effect will be mutual disassociation of any complex molecules of the pure components. As the characters of the two substances diverge, the extent of compound formation will become appreciable. The complexes in this case will be limited to those of the simplest type AB·CD. In the third case, where the two substances are decidedly diverse, there will be more extensive compound formation. The complexes formed will be not only of the simplest type AB·CD but also of the larger molecular species $(AB)_x(CD)_y$. The solution will be a good conductor as disintegration of these complexes into ions of opposite charge takes place readily. It is thus found to be the rule that two features are essential in a solution of high specific conductivity:

(a) unsaturation which renders possible the formation of complexes, and
(b) diversity in the character of the two components.

A recent investigation[1] has been completed in this laboratory upon the conductivities of non-aqueous systems and an attempt has been made to extend our knowledge of the equilibrium existing between ionized and un-ionized portions. The systems investigated were those of acids with esters, acids with ketones, and acids with other acids. Acetic acid and trichloracetic acid were chosen as a typically weak and strong acid, respectively, ethyl acetate as the ester, and acetone and acetophenone as the ketones, the first being decidedly basic and the second less so.

In the system acetic-ethyl acetate, where the two components are not very different in character, compound formation is inconsiderable and the conductivities are practically the same as those of the pure components. Trichloracetic and ethyl acetate are widely diverse and therefore form a stable compound (M.P.–27°) and give a fairly sharp maximum in the conductivity curve of their mixtures. In the systems of the two ketones with the acids, the decided basic character of the ketones is the cause of more extensive compound formation than occurs in the case of the ester. The compounds formed with the trichloracetic are ionically unstable and give good conducting solutions due partly to the low viscosity of the acetone. Even with acetone and acetic acid the conductivities are comparable with those of the ester and the strong acid.

Since acetophenone is less basic than acetone, the conductivities of the systems acetophenone-trichloracetic and the acetophenone-acetic are less than those with acetone. With trichloracetic, acetophenone forms an equimolecular addition compound of M.P.26°. A very flat maximum is obtained due to the high degree of dissociation of the complex. In the system acetic-trichloracetic an addition compound is formed but the conductivity does not reach a very high value due to the acidic character of both of the compounds.

[1] Kendall and Gross, J. A. C. S. (1920).

In all the results obtained the factor which has an exceedingly important influence upon the conductivity is the viscosity. It is not right to compare conductivities directly when the viscosity varies as much as 1000% in certain systems, owing to the difference in the mobility of the ions. Walden[1] has shown that the product of ionic mobility by viscosity is approximately a constant and if this product is plotted against the molecular per cent. of the system, the maximum should be the true indication of the solution of maximum ionization.

The object of this research has been to make an accurate examination of the viscosities of the above liquids and their mixtures in order to render possible a more strictly quantitative determination of the conditions existing in the solutions. The viscosity results can be utilized in two ways:

(a) by direct examination of the shape of the viscosity curves,
(b) by application of viscosity data to the conductivity curves.

These two points will be taken up separately.

VISCOSITY CURVES IN NON-IDEAL SOLUTIONS

Thus far no ideal formula has been found for viscosity[2]. That it is not an additive property is illustrated by viscosity composition curves of binary liquid mixtures where the viscosities are uniformly lower than the mixture rule would indicate. Until the ideal equation is known, no quantitative conclusions can be drawn from the study of non-ideal systems such as those under investigation. Findlay[3] and Denison[4] claim that the composition of the complexes formed is indicated by the position of maximum divergence from the normal, but this rule is obviously useless as long as the normal is unknown. It has been conclusively shown that the normal cannot be assumed to be linear[5]. In non-ideal systems where it is recognized that

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[1] Walden, Z. physik. chem. 55, 207 (1906).
[2] Dunstan and Thole. "The Viscosity of Liquids." Longmans Green & Co. (1913).
Kendall and Monroe 39, 1787 (1917).
[3] Findlay, Z. physik. chem. 69, 203 (1909).
[4] Denison, Trans. Faraday Soc. 8, 20 (1912).
[5] Dawson, Ann. Reports Chem. Soc. 13, 17 (1916).

there is interaction between the components, a minimum is considered to indicate the disassociation of an associated liquid and a maximum the formation of an addition compound. As it is well known that in the systems under investigation both association and compound formation occur, it is to be expected that the two processes will have an opposed effect upon the shape of the curves. The disassociation of the associated substances will tend to lower the viscosity as the large molecules are breaking up into smaller ones, and the result will be a sagging curve. This result, however, will in most cases be partly or entirely counterbalanced by the formation of complexes of higher viscosity than the pure substances. From the shape of the curves observed the approximate amount of disassociation and compound formation can be estimated.

APPLICATION OF VISCOSITY DATA TO CONDUCTIVITY CURVES

There is a general rule that the viscosity increases with an increase in the molecular complexity or with association. When ionically unstable complexes are formed in a solution, therefore, the increased conductivity is partly balanced by the increased viscosity. The result will be a change in the position of the maximum on the conductivity curve in the direction of the less viscous compound. Therefore, the position of the maximum can not be taken as the constitution of the compound formed without taking into consideration the viscosity of the system.

As observed above, Walden has formulated a rule for correcting the conductivity of solution by means of the viscosity. He worked with dilute solutions of tetramethyl ammonium iodide of varying concentrations and found that the product of equivalent conductivity by viscosity is approximately a constant:

$$\Lambda\eta = \text{constant},$$

$$\text{i. e. (ionic mobilities)} \times \eta = \text{constant}.$$

In the work done by Kendall and Gross, the specific conduc-

tivity, k, was determined for the various non-aqueous solutions of finite concentrations. Now the specific conductivity k = (ionic concentrations in fixed volume) x (mobility of the ions) x constant. The application of Walden's rule to this results in the expression $k\eta$ = ionic concentrations in fixed volume) x constant. In order to reduce this to molecular ratios, we must introduce the molecular volume[1] of each solution, and finally obtain $k\eta \times$ (molecular volume)=(fraction of mole ionized) x constant. This final product, $k\eta \times$ molecular volume, is then plotted against the molecular per cent. of the solution and the position of the maximum should be the true indication of the composition of the addition compound. In general, if the compound formed is complex and ionically unstable, the maximum ionization will occur in the solution of maximum compound formation, i. e. in the solution represented by the composition of the compound. There is the possibility, however, that simple compounds may exist in the mixture which are ionically very stable. A well known example may be taken from the system H_2SO_4—H_2O. In the conductivity curve for this system, a minimum is obtained where the molecular composition is fifty per cent. The simple addition compound $H_2SO_4 \cdot H_2O$ is known to exist but as it is ionically quite stable, it gives a solution of minimum conductivity. On either side of this minimum more complex compounds exist which are ionically less stable. It must be noted, therefore, that all compounds formed will not be represented equally on the final diagrams, but that the more complex (with greater ionic instability) will be emphasized as maxima in the coudnctivity curves.

Experimental:

For the experimental work the apparatus was used which was devised by Bingham[2] and followed by Kendall[3] and Mon-

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[1] The molecular volume is found from the relation

$$\text{Molecular Volume} = \frac{\text{Average Molecular Weight}}{\text{Density}}$$

[2] Bingham, Ind. Eng. Chem. 6, 233 (1914).
[3] Kendall and Monroe 39 1787 (1917).

roe in a previous investigation from this laboratory. A low-pressure reservoir was connected through a water-manometer to the viscometer and evacuated with a filter pump. The manometer was also connected to another reservoir of slightly lower pressure than the first by which the pressure could be kept constant and leakage avoided. The water levels in the manometer were read from a steel tape fixed on a plate glass mirror. The viscometer was clamped in an insulated glass thermostat regulated electrically to $25^0 \pm .02^0$. Great precaution was taken to keep the viscometer dust free by cleaning with chromic acid, washing with distilled water, alcohol, and ether, and drying with a current of dry air. The procedure was the same as that employed in the previous investigation. The mixture was weighed in a standardized 20 cc. flask and the density thus obtained. The contents were shaken thoroughly and the necessary amount pipetted into the viscometer which was immediately connected with the low pressure reservoir. The time of flow of the liquid past two fixed marks was observed and several duplicate runs were made in reverse directions and the average was taken.

Standardization of Apparatus:

The viscometers were standardized by means of water at 25^0 as in the previous investigations. The absolute value for water $\eta = .008946$ was used. The viscosity formula for any instrument is:

$$\eta = \frac{\pi g r^4 p t}{8 V l} - \frac{1.12 n \rho V}{8 \pi t l}$$

(where g = acceleration of gravity; r = radius of capillary; v = transpiration volume; l = length of capillary; n = number of capillaries and ρ = density of liquid). This reduces to the form

$$\eta = C p t - C' \rho / t$$

As the second term is a correction term, C' which equals $1.12 n V / 8 \pi l$ is obtained with sufficient accuracy by direct measurement. The value for C is then found from experiment with a standard liquid. Bingham[1], Schlesinger, and Coleman have shown that to obtain constant values for C, a correction

must be made to the observed pressure. This is due to the fact that the pressure p_0 given by the manometer must be corrected for the head of the liquid to give the true average pressure p. This value is given by the relation:

$$p = 2h\rho / \log_e \frac{p_0 + h\rho}{p_0 - h\rho}$$

(where h is the maximum head of the liquid in the manometer).

RESULTS FOR VISCOSITY DETERMINATIONS

System Acetic Acid-Ethyl Acetate.

The ethyl acetate was purified by successive fractionations using a stillhead of pyrex glass of improved design with the corks carefully protected to prevent contamination. All thermometers used were carefully standardized and the necessary stem and barometric corrections applied. The fraction employed boiled at $77^{\circ}.1 \pm^{\circ}.05$.

The best C.P. glacial acetic acid was obtained and its freezing point determined. From this the water content was calculated and the theoretical amount of acetic anhydride was added. The mixture was hydrolyzed by refluxing at the boiling point for thirty hours, care being taken to exclude moisture. The acid was then fractionated to eliminate impurities other than water. The fraction boiling at $117^{\circ}.8 \pm .1^{\circ}$ was the one taken. It froze at $16^{\circ}.57 \pm^{\circ}.05$.

Mol. % Acetic Acid	Densities	Viscosities
100.00	1.0499	0.01121
87.42	1.016	0.009430
80.11	1.001	0.008590
69.88	0.9860	0.007668
59.96	0.9697	0.006890
49.85	0.9557	0.006289
39.90	0.9417	0.005762
30.37	0.9308	0.005331
20.70	0.9211	0.004949
10.49	0.9092	0.004590
0.00	0.8948	0.004236

[1] Bingham, Schlesinger, and Coleman, J. Am. Chem. Soc. 38, 27 (1916).

The system acetic acid-ethyl acetate gives an approximately normal curve although it is well known that acetic acid is a highly associated liquid. The formation of a small amount of a compound of greater viscosity than the pure components must therefore be assumed to counterbalance the lowering in viscosity produced by the disassociation of the associated acetic acid. The table for this system is given above and the curve will be found in figure I.

System Trichloracetic Acid-Ethyl Acetate

C.P. trichloracetic acid was dissolved in benzene and then crystalized out by rapid cooling in a freezing mixture. The crystals were washed with cold benzene which was quickly drained off. The remaining crystals were melted and poured hot into a crystalizing dish over 99% H_2SO_4 in a vacuum dessicator. When cooled the solution crystalized out and the benzene was taken up by the acid which was sulphonated. Pure trichloracetic acid was thus obtained which gave a melting point of 59°.2.

Mol. % Acetate	Densities	Viscosities
100.00	0.8948	0.004236
88.82	0.9972	0.005878
81.60	1.045	0.007309
71.93	1.123	0.01001
61.54	1.202	0.01449
51.22	1.295	0.02176
38.58	1.376	0.03467
29.92	1.454	0.04709

In the systems where one component is trichloracetic acid, the viscosity curves at 25° could be carried only as far as about seventy-five molecular per cent. of the acid, due to the fact that it is a solid at ordinary temperatures. To gain a general idea of the viscosity of the pure substance at 25°, measurements were made with an Ostwald viscometer at 60° and 70° and the results extrapolated to 25°. It was found that the viscosity at 25° of the pure acid is 0.0683. This determination was only very approximate, due to errors in measurement using the Ostwald viscometer and to the fact that the change in viscosity with temperature is assumed to be a linear function.

It is, however, sufficient for the prediction of maxima in all the systems examined where one component is trichloracetic acid.

Pure Trichloracetic:

Density	Viscosity
1.595 (60°)	0.03971 (60°)
1.588 (70°)	0.03149 (70°)
	0.0683 (25°)

The addition of trichloracetic to ethyl acetate causes a rapid rise in the curve due to the extensive formation of complexes of high viscosity. Although the curve could be carried only to seventy per cent. of the acid, the value for the viscosity of pure trichloracetic indicates that a maximum exists, followed by a very sudden fall of the curve on the side towards the acid. The table for this system is given above and the curve will be found in figure III.

SYSTEM ACETIC ACID AND ACETONE

Mol. % Acetic	Densities	Viscosities
100.00	1.0499	0.01121
90.37	1.015	0.01036
80.15	0.9907	0.009213
69.68	0.9609	0.008026
59.73	0.9333	0.006994
49.86	0.9064	0.006098
40.49	0.8847	0.005350
30.25	0.8568	0.004636
20.35	0.8351	0.004046
9.96	0.8089	0.003496
0.00	0.7872	0.003065

The acetone was purified by the formation of the bisulphite addition compound and then hydrolyzed by distilling off the pure acetone from the crystals.

As both components of this system are known to be highly associated, a minimum would be expected. The actual curve, however, does not sag but is slightly above the normal. There is a fairly wide divergence in character between acetic acid and acetone and the consequent compound formation raises the curve above the normal but is not sufficient to cause a maximum. The table for this system is given above and the curve in figure I.

SYSTEM TRICHLORACETIC ACID AND ACETONE

Mol. % Acetone	Densities	Viscosities
100.00	0.7872	0.003065
95.16	0.8541	0.003680
86.84	0.9342	0.004855
74.57	1.073	0.008156
61.74	1.209	0.01433
49.52	1.319	0.02571
40.29	1.400	0.03829
28.25	1.483	0.05808

As acetone and trichloracetic are very widely diverse in character, the extensive formation of complexes causes the curve to rise rapidly, more than counterbalancing any lowering in viscosity due to the disassociation of the highly associated acetone. The maximum was not reached but one can be predicted from the value of the viscosity of pure trichloracetic, followed by a sudden descent on the acid side of the curve. The table for this system is given above and the curve in figure III.

SYSTEM ACETIC ACID-ACETOPHENONE

Mol. % Acetic	Densities	Viscosities
0.00	1.0263	0.01681
9.98	1.0272	0.017407
21.07	1.0287	0.017536
29.35	1.0300	0.01742
42.53	1.0325	0.01703
48.85	1.0338	0.01668
60.03	1.0365	0.01598
69.98	1.0390	0.01524
80.02	1.0420	0.01420
90.13	1.0453	0.01293
100.00	1.0499	0.01121

Acetophenone was first dehydrated with phosphorous pentoxide for several days and then fractionated under ordinary pressure. Care was taken to pour off the phosphorous pentoxide before distilling to avoid the formation of any benzoic acid. The fraction boiling at $202^{\circ}.3 \pm .1^{\circ}$. was used.

The curve obtained for this system is above the normal and reaches a flat maximum at twenty molecular per cent. of the acid. There is less diversity in character between the com-

ponents than for the system acetone-acetic acid and consequently less compound formation. Acetophenone, however, is associated to a smaller degree than acetone and there will be less lowering in viscosity due to disassociation. The formation of complexes will thus cause the curve to rise more rapidly than for the system with acetone-acetic. The table is given above and the curve in figure II.

SYSTEM TRICHLORACETIC ACID AND ACETOPHENONE

Mol. % Acetophenone	Densities	Viscosities
100.00	1.026	0.01681
91.04	1.076	0.02112
86.00	1.103	0.02402
78.79	1.146	0.02931
70.61	1.192	0.03735
59.10	1.268	0.05540
51.24	1.317	0.07349
42.06	1.386	0.09330
31.85	1.442	0.1115

As in the other systems with trichloracetic, the viscosity increases rapidly due to the formation of complexes. A point of inflection is observed at about fifty molecular per cent. The value for the viscosity of pure trichloracetic indicates the existence of a maximum of high viscosity with a rapid descent on the acid side of the curve. The table for this system is given above and the curve in figure IV.

SYSTEM ACETIC ACID AND TRICHLORACETIC

Mol. % Acetic	Densities	Viscosities
100.00	1.049	0.01121
92.63	1.129	0.01532
82.23	1.223	0.02228
67.91	1.337	0.03362
56.52	1.409	0.04346
47.38	1.457	0.05176
41.47	1.491	0.05859
34.19	1.508	0.06854

Acetic and trichloracetic are acids of widely different strengths and consequently compound formation may be predicted. The curve rises rapidly and the complexes found

cõunterbalance any lowering in viscosity due to disassociation of the associated acetic. As in the other curves with trichloracetic the presence of a maximum is indicated. The table is given above and the curve in figure IV.

CONCLUSIONS FROM VISCOSITY CURVES

It may be concluded from the discussion of the individual systems that the results are in close agreement with the theoretical basis developed at the beginning of this paper. Interaction between the components has been shown to occur in each system examined, the complexity and stability of the compounds formed depending upon the difference in character of the pure substances. Where the difference is slight a flat maximum is obtained due to the high degree of dissociation of the complex (e. g. the system acetic acid and acetophenone). With wide diversity between the components, extensive compound formation causes a rapid rise of the viscosity curve, resulting in a sharp maximum, as is illustrated by any curve using trichloracetic. Compound formation is sometimes totally obscured by disassociation of the pure substances, as in the case of acetic acid and ethyl acetate where an approximately normal curve is obtained.

RESULTS FOR CORRECTED CONDUCTIVITY CURVES

SYSTEM ACETIC ACID-ETHYL ACETATE

Mol. % Acid	k x 10^7	Viscosity	Density	k η (Mol. Vol.) x 10^7
0.00	0.01	0.004236	0.895	0.004
23.52	0.05	0.005037	0.923	0.022
49.27	0.12	0.006265	0.955	0.058
77.87	0.20	0.008329	0.998	0.11
100.00	0.24	0.01121	1.050	0.15

The corrected conductivity data for this system gives practically a straight line, indicating that the amount of compound formation is insignificant. The table for this system is given above.

SYSTEM TRICHLORACETIC-ETHYL ACETATE

Mol. % Trichloracetic	k x 10^7	Viscosity	Density	k η (Mol. Vol.) x 10^7
0.00	0.01	0.004236	0.895	0.004
4.93	1.10	0.004896	0.935	0.529
9.80	2.59	0.005611	0.975	1.43
14.36	4.36	0.006436	1.012	2.75
19.55	5.94	0.007536	1.053	4.37
23.56	7.32	0.008636	1.086	6.14
27.31	8.37	0.009736	1.117	7.93
30.07	9.12	0.01061	1.138	9.41
33.06	9.62	0.01177	1.167	10.96
36.67	9.95	0.01342	1.192	12.96
42.05	10.05	0.01645	1.234	16.04
48.05	9.67	0.02095	1.280	19.67
51.52	9.19	0.02415	1.306	21.56
54.34	8.74	0.02679	1.329	22.7
57.22	8.11	0.02976	1.351	23.4
59.07	7.68	0.03174	1.366	23.7
63.16	6.82	0.03669	1.398	24.3
72.63	3.93	0.05076	1.470	19.4
79.12	2.24	0.06013	1.514	13.12

The curve for this system gives a fairly sharp maximum at about sixty-four molecular per cent. of the acid. The position of the maximum suggests that the compound chiefly responsible for the high conductivity is composed of two molecules of acid and one of ethyl-acetate. The table for this system is given above and the curve in figure V.

SYSTEM ACETIC ACID-ACETONE

Mol. % Acetic	k x 10^7	Viscosity	Density	$k\eta$ (Mol. Vol.) x 10^7
0.00	0.58	0.003065	0.787	0.13
12.56	3.02	0.003619	0.816	0.781
20.27	3.46	0.004026	0.835	0.975
28.65	4.19	0.004539	0.854	1.31
39.45	4.42	0.005297	0.879	1.57
46.03	4.58	0.005985	0.895	1.81
51.04	5.08	0.006142	0.908	2.03
64.92	4.80	0.007487	0.946	2.26
71.43	4.32	0.008196	0.965	2.18
81.10	3.12	0.009296	0.992	1.74
92.23	1.33	0.01038	1.025	0.807
100.00	0.26	0.01121	1.050	0.17

The corrected conductivity curve for this system gives a maximum at sixty-six molecular per cent. of the acid, again suggesting the formation of a two-one ionically unstable addition compound. The table for this system is given above and the curve in figure VII.

SYSTEM TRICHLORACETIC ACID-ACETONE

Mol. % Acid	k x 10^7	Viscosity	Density	$k\eta$ (Mol. Vol.) x 10^7
0.00	0.58	0.0030653	0.787	0.13
3.37	88.61	0.003431	0.823	22.75
6.76	128.4	0.003858	0.862	37.45
10.05	163.0	0.004224	0.900	52.50
12.52	198.5	0.004590	0.928	69.93
16.28	214.5	0.005322	0.970	88.52
19.53	222.9	0.006054	1.007	105.4
23.04	224.8	0.007091	1.045	125.6
26.02	218.9	0.008189	1.080	141.9
28.57	205.1	0.009165	1.107	149.7
31.81	183.4	0.01056	1.143	156.2
40.04	144.1	0.01563	1.226	184.1
47.32	118.0	0.02210	1.295	217.3
54.17	95.72	0.03021	1.355	245.7
59.74	73.84	0.03815	1.400	243.4
65.79	54.39	0.04808	1.444	230.6
72.47	33.06	0.05918	1.486	177.0
	20.23			

The corrected conductivity curve for this system gives a sharp maximum, the value of which is the highest for any of the systems examined. This is to be expected since the greatest difference in character between the two components is here observed. The table for this system is given above and the curve in figure VI.

SYSTEM ACETIC ACID-ACETOPHENONE

Mol. % Acetic	k x 10^7	Viscosity	Density	$k\eta$ (Mol. Vol.) x 10^7
0.00	0.9	0.01681	1.0263	1.8
6.91	2.86	0.01720	1.0268	5.56
16.39	3.33	0.01754	1.0280	6.26
25.39	3.51	0.01749	1.0293	6.25
33.29	3.58	0.01734	1.0306	6.03
40.98	3.46	0.01709	1.0322	5.47
49.55	3.44	0.01665	1.0340	5.01
57.22	3.20	0.01615	1.0358	4.29
65.87	2.83	0.01556	1.0379	3.41
69.68	2.59	0.01526	1.0389	2.97
77.20	2.26	0.01445	1.0411	2.32
82.79	1.75	0.01389	1.0428	1.60
90.74	1.11	0.01283	1.0454	0.890
100.00	0.24	0.01121	1.0499	0.15

The corrected curve for this system gives a fairly flat maximum at thirty-three molecular per cent. of the acid, suggesting the existence of an ionically unstable complex of the composition one molecule of acid and two of acetophenone. The table for this system is given above and the curve in figure VII.

SYSTEM TRICHLORACETIC-ACETOPHENONE

Mol. % Trichloracetic	k x 10^7	Viscosity	Density	$k\eta$ (Mol. Vol.) x 10^7
0.00	0.9	0.01681	1.026	1.8
6.83	11.39	0.02001	1.062	26.38
14.04	15.96	0.02411	1.102	44.05
24.60	20.10	0.03191	1.162	72.17
36.92	21.35	0.04741	1.241	110.95
44.15	21.41	0.06271	1.289	145.0
48.42	21.66	0.07281	1.318	168.8
53.23	22.38	0.08341	1.349	198.1
59.94	22.57	0.09741	1.394	230.3
66.64	20.84	0.1087	1.436	234.9
72.42	16.88	0.1166	1.472	202.4
71.37	17.77	0.1152	1.466	210.8

The curve for this system rises rapidly, giving a sharp maximum with a value nearly as high as that observed for trichloracetic and acetone. The table for this system is given above and the curve in figure VI.

SYSTEM ACETIC-TRICHLORACETIC

Mol. % Acetic	k x 10^7	Viscosity	Density	$k\eta$ (Mol. Vol.) x 10^7
39.61	2.25	0.06077	1.490	11.3
47.64	3.80	0.05165	1.458	15.4
55.13	5.64	0.04427	1.415	18.8
62.01	7.10	0.03821	1.376	19.6
68.25	8.08	0.03299	1.334	18.6
72.33	8.31	0.02975	1.303	16.8
76.28	8.05	0.02669	1.272	14.3
81.28	6.37	0.02297	1.230	9.42
89.57	3.67	0.01733	1.157	3.89
95.14	1.67	0.01385	1.102	1.36
100.00	0.26	0.01121	1.050	0.17

The difference in character between the two acids is sufficient to cause considerable compound formation as is shown by the existence of a fairly sharp maximum. The maximum occurs at sixty molecular per cent. of acetic, suggesting that the most ionically unstable complex formed has the composition three molecules of acetic and two of trichloracetic. The table for this system is given above and the curve in figure V.

CONCLUSIONS TO CORRECTED CONDUCTIVITY CURVES

The complexes suggested by the corrected conductivity curves of the above systems differ in composition from those isolated by the freezing point method. This fact is not surprising as the more complex addition compounds are probably formed in too small a quantity to be isolated in the solid state. They will appear, however, as maxima in the conductivity curves as they are ionically much less stable than the simplest complex containing one molecule of each component. It is observed above that in the majority of cases the maximum comes at the position sixty-six molecular per cent. of the acid,

suggesting that the ionically unstable complex is composed of two molecules of acid and one of the other component.

As stated in a previous section, these corrected conductivity curves have been obtained by application of Walden's rule, namely, that the product of viscosity by equivalent conductivity is a constant. In his work with dilute solutions of tetramethyl ammonium iodide in twenty-six different solvents he found that the product $\Lambda\eta$ was constant only within the limits of five per cent. error. This fairly large error may account for some of the discrepancies of the curves and for a variation of as much as two or three per cent. in the position of the maximum.

As the composition changes, the concentration of the various compounds formed will also change and the complexity of the ions formed from these compounds will vary with the molecular per cent. of the system. The resulting variation in the ionic velocities will, in all probability, introduce a slight error and the effect upon the position of the maxima will be small.

The results obtained from these corrected conductivity curves substantiate the conclusions drawn from the work of Kendall and Gross. They show that compound formation between the two acids and the other organic compounds examined is the general rule and that the complexity and consequently the ionic instability of the compounds formed increases with increasing difference in character of the components.

SUMMARY

(1) The factors affecting the viscosities of non-ideal binary mixtures have been discussed and applied to cases of association and compound formation in solution.

(2) In order to test the conclusions drawn, the viscosities of non-aqueous solutions of the type acid—x (where x is an ester, ketone, or acid) have been determined through a wide range of concentrations.

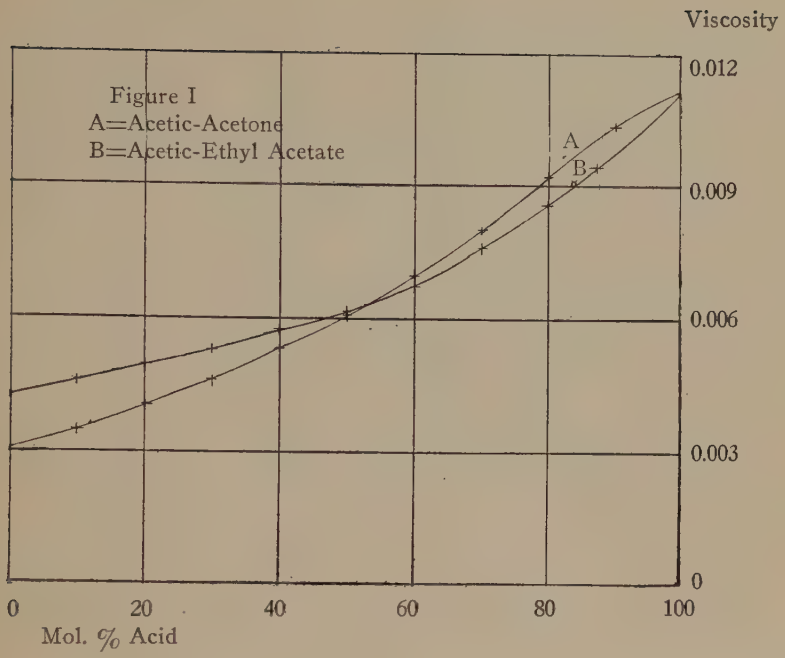
(3)An examination of the viscosity curves obtained has shown them to be in close agreement with the hypothesis advanced.

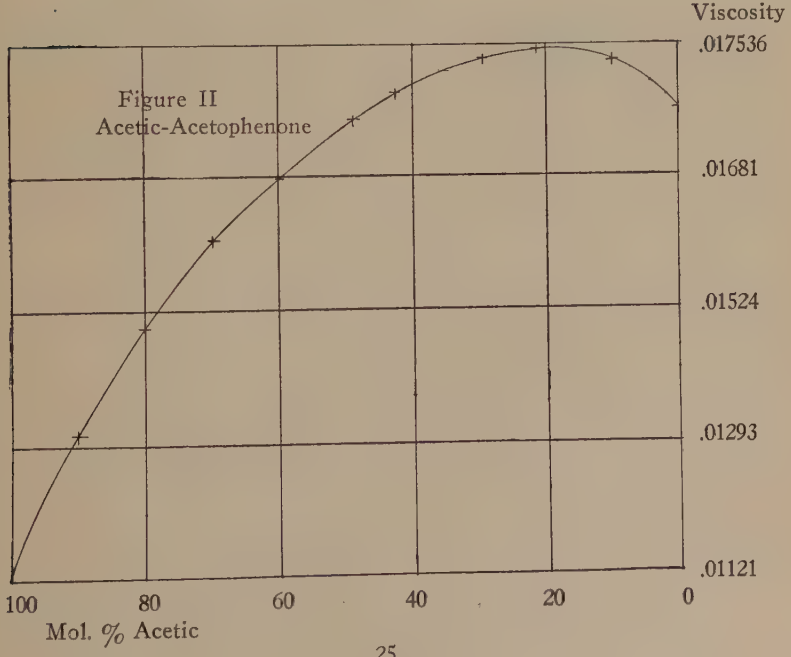
(4) An application of the viscosity data has been made to the conductivity curves determined for the same systems.

(5) Conclusions have been drawn from the corrected conductivity curves as to the nature and extent of the ionically unstable complexes formed in the solutions.

VITA

Elizabeth Brakeley was born in Freehold, New Jersey, on April 30, 1894, and attended the grade and high schools of that town. After one year spent at the Baldwin School, Bryn Mawr, Pennsylvania, she entered Bryn Mawr College in September, 1912, and from that institution received successively the degrees A. B. and A. M. in 1916 and 1917. She entered Columbia University in September, 1917, and spent the following two and a half years in graduate study. She was an assistant in physical chemistry in Columbia University during the year 1919-1920.


Viscosity
Figure I
A=Acetic-Acetone
B=Acetic-Ethyl Acetate
A
B
0.012
0.009
0.006
0.003
0
0
20
40
60
80
100
Mol. % Acid


Viscosity
Figure II
Acetic-Acetophenone
.017536
.01681
.01524
.01293
.01121
100
80
60
40
20
0
Mol. % Acetic

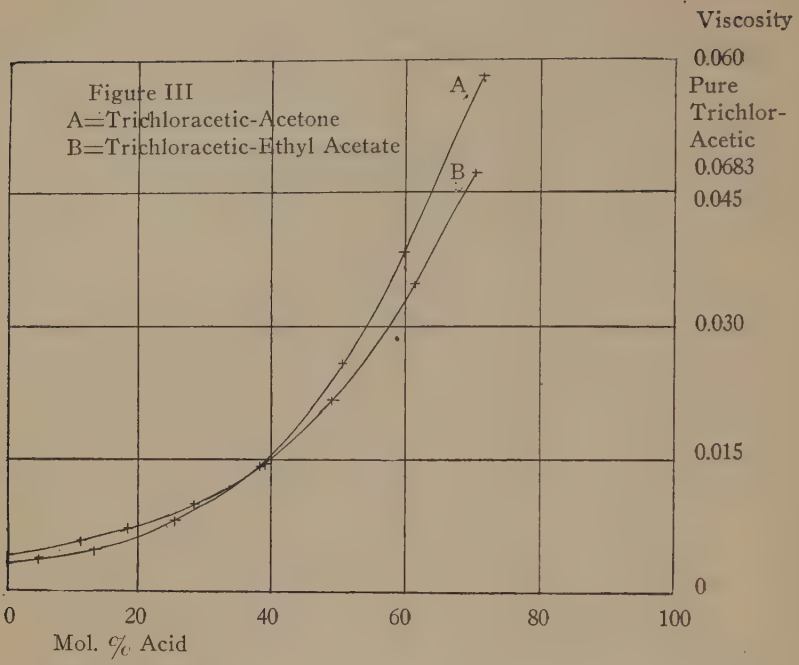


Figure III
A=Trichloracetic-Acetone
B=Trichloracetic-Ethyl Acetate

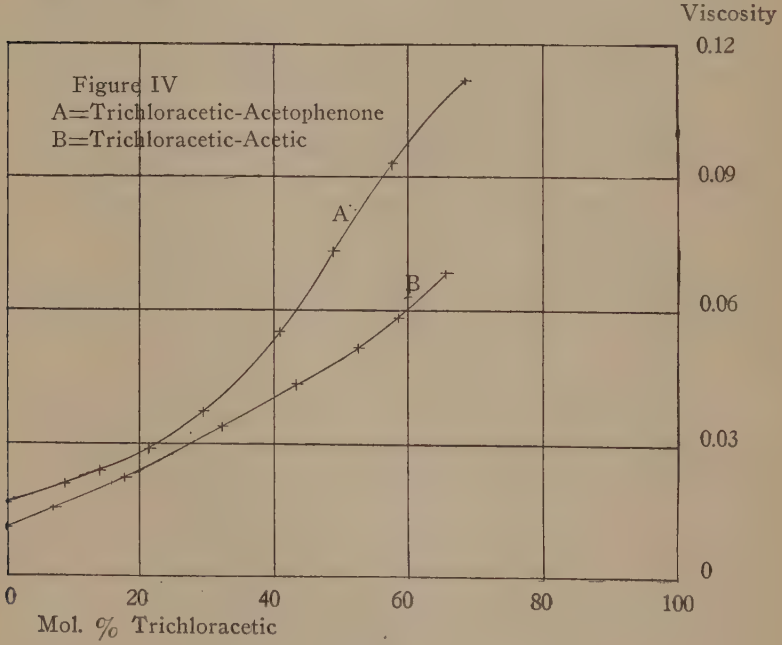


Figure IV
A=Trichloracetic-Acetophenone
B=Trichloracetic-Acetic

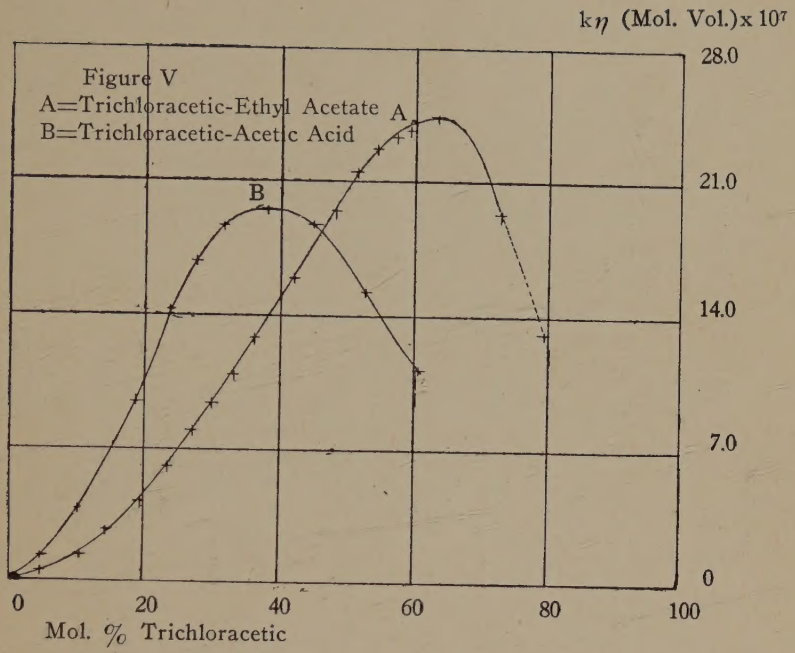


Figure V
A=Trichloracetic-Ethyl Acetate
B=Trichloracetic-Acetic Acid

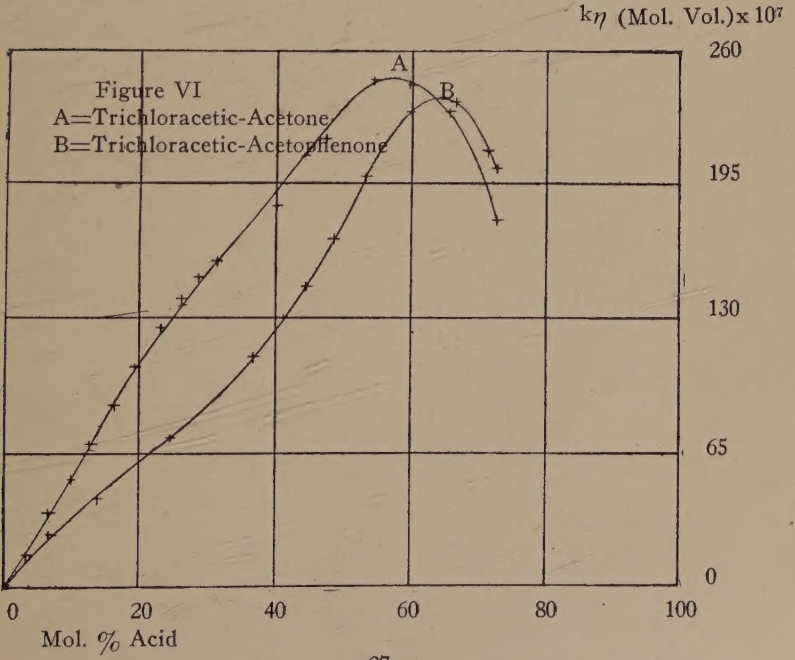


Figure VI
A=Trichloracetic-Acetone
B=Trichloracetic-Acetophenone

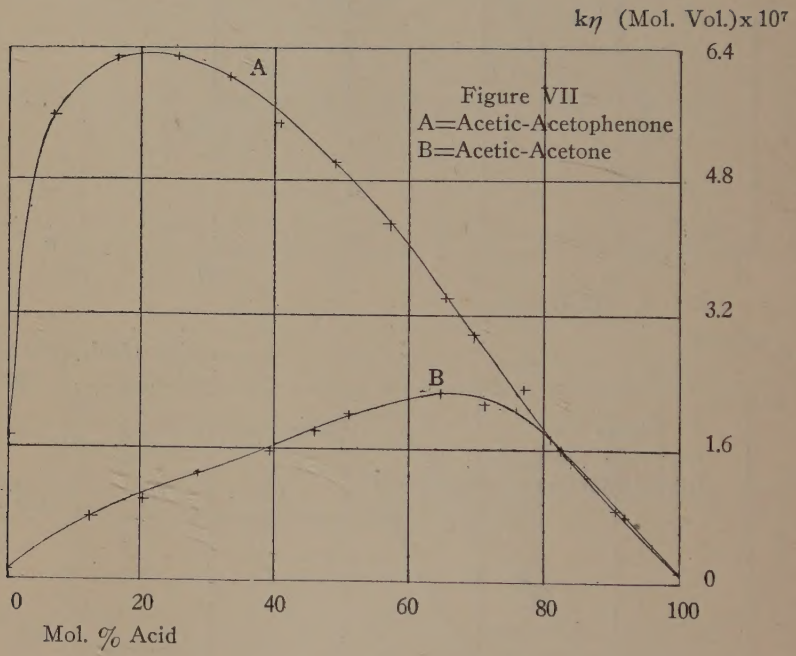


Figure VII
A=Acetic-Acetophenone
B=Acetic-Acetone